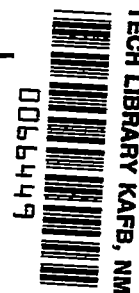


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TECHNICAL NOTE 3384

EFFECT OF HYDROCARBON STRUCTURE ON REACTION PROCESSES

LEADING TO SPONTANEOUS IGNITION

By Donald E. Swarts and Charles E. Frank

University of Cincinnati



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TECHNICAL NOTE 3384

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SUMMARY

Previous work showed that heptane and isooctane not only differed greatly in respect to their susceptibilities to vapor-phase oxidation but that the nature of the oxidation products was also different. These facts were interpreted on the basis of the temperature required for oxidative attack and on the thermal stability of the alkyl and peroxy radicals obtained. This work has been extended to other aliphatic hydrocarbons in the present investigation.

Experiments with 2,2,5-trimethylhexane, which differs from isooctane in having one more methylene group, show that this compound occupies an intermediary position between isooctane and n-heptane in susceptibility to oxidation. The addition of a methylene group reduces the resistivity of a hydrocarbon to oxidation.

The 2,2-dimethylbutane, which contains two secondary C-H bonds, is more easily oxidized than its isomer, 2,3-dimethylbutane, which contains two tertiary C-H bonds. This apparent anomaly may be due to the fact that tertiary C-H bonds in 2,3-dimethylbutane are sterically shielded from oxygen attack by the adjacent methyl groups.

In the temperature range from 350° to 450° C 3-heptene gave oxidation products similar to those from n-heptane but showed greater resistance to oxidative attack. At temperatures of 500° to 550° C, isobutene appeared slightly more susceptible to oxidation than isobutane. Possible explanations for these observations are suggested.

When a reaction tube with 1/4-inch inside diameter was used, isooctane gave oxidation products similar to those previously reported with the 1/16-inch tube. However, for a given contact time the extent of reaction and the danger of explosion were much greater in the larger diameter tube. These results illustrate the importance of a high surface-to-volume ratio in controlling vapor-phase oxidation processes.

INTRODUCTION

Previous work on the investigation of the reaction processes leading to the spontaneous ignition of hydrocarbons (ref. 1) showed that the structure of the hydrocarbon influences the ease of oxidative attack and the thermal stability of the alkyl and peroxy radicals initially formed. Other important factors controlling the rate and course of the vapor-phase oxidation of hydrocarbons are temperature, contact time, and "wall effect." The effect of the type of C-H bonding in the molecule was shown previously by comparing the intermediate oxidation products of isooctane and n-heptane. Preliminary experiments with isobutane and 2,2,5-trimethylhexane provided further evidence for the order of C-H stability. The order of increasing resistance to oxidative attack of the above compounds was found to be n-heptane, 2,2,5-trimethylhexane, and isooctane.

The present study has had as its objective a comparison of the behavior of other hydrocarbons with those previously studied. A study of the behavior of olefins and some exploratory work on the effect of the ratio of surface to volume on the extent of oxidation in the early stages was also included. This investigation was conducted at the Applied Science Research Laboratory of the University of Cincinnati under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

DESCRIPTION OF APPARATUS

The apparatus used in this investigation has been described in a previous report (ref. 1) and consists essentially of three parts: (1) The hydrogen-oxygen mixing tube, held at constant temperature during the experiment, (2) the oxidation chamber, composed of a 13-inch-long glass tube with either 1/16- or 1/4-inch inside diameter in an electrically heated furnace, and (3) cold traps (-70°C) for rapid quenching of the reaction products. A final scrubber containing an aqueous solution of 2,4-dinitrophenylhydrazine reacts with volatile carbonyl compounds.

Cylinder oxygen was dried by passing it through sulfuric acid and the oxygen was then conducted through a calibrated flowmeter and into the hydrocarbon held at a constant temperature so as to obtain a known fuel-oxygen mixture. Temperatures were selected to secure a stoichiometric mixture of fuel and oxygen in all experiments. With the less volatile compounds tested, for example, isooctane and 2,2,5-trimethylhexane, a refluxing vapor bath was utilized to maintain the hydrocarbon at the necessary temperature. However, with the more volatile compounds, for example, 2,2-dimethylbutane and 2,3-dimethylbutane, the proper temperature of the hydrocarbon was obtained by circulating coolant at a

controlled temperature around the bubbler tube. The oxygen was also precooled to the same temperature before mixing. With the gaseous compounds, for example, isobutane and isobutene, a second calibrated flowmeter was used to measure the hydrocarbon, and thorough mixing was obtained by the turbulent flow of the fuel-oxygen mixture through a 2-inch section of stainless-steel column packing and a fritted-glass scrubber tube. The fuel-oxygen mixture was then passed through the reaction chamber at a selected contact time and temperature and the reaction products were quenched in the cold traps.

For the most part the oxidation was conducted in a 1/16-inch-inside-diameter glass tube, where a large "wall effect" would assist in controlling and quenching the reaction during the early stages. To examine the effect of a larger diameter tube on the oxidation of isooctane, a 1/4-inch-inside-diameter tube was substituted for the 1/16-inch-inside-diameter tube. The temperature distribution throughout the 1/4-inch-inside-diameter tube was measured at various temperature settings as before (ref. 1). From the curves obtained (fig. 1) it is apparent that there is little change in the temperature distribution from the 1/16-inch-inside-diameter tube.

TEST PROCEDURE

The reaction mixture from each experiment was quenched and analyzed as described previously (ref. 1). To analyze for the various reaction products the water-soluble components were separated from the organic-soluble components by several extractions of the mixture with water. The water phase was analyzed for total peroxide, hydrogen peroxide, total carbonyls, aldehydes, and acids. The organic phase was tested for peroxides, carbonyl compounds, and olefins.

Total Peroxides

Total peroxides were determined iodometrically. A piece of dry ice was added to 10 cubic centimeters of glacial acetic acid in a titration flask to sweep out the air. After excess potassium-iodide solution was added to the sample and it was allowed to stand in the dark for 1/2 hour, the liberated iodine was titrated with 0.1-normal sodium thiosulfate.

Hydrogen Peroxide

Hydrogen peroxide was determined colorimetrically by the reaction with titanium-sulfate reagent (ref. 2). The percent light absorption at 400 millimicrons was measured with a spectrophotometer and the value of

the hydrogen-peroxide content corresponding to this percent absorption was read directly from a calibrated chart.

Carbonyl Compounds

Carbonyl compounds were determined gravimetrically by precipitation of the 2,4-dinitrophenylhydrazones using the reagent solution described by Shriner and Fuson (ref. 3).

Olefins

Olefins were determined by hydrogenation as described by Siggia (ref. 4). Platinum-oxide catalyst was used. The peroxides and carbonyl compounds must be removed prior to this determination.

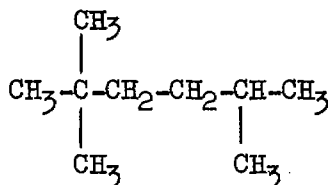
Aldehydes and Acids

Aldehydes were determined as the derivative of methone (ref. 5). Acids were determined by titration with 0.1-normal sodium hydroxide using phenolphthalein as indicator.

RESULTS AND DISCUSSION

Oxidation of Various Hydrocarbons

2,2,5-trimethylhexane.— Preliminary data for the oxidation of 2,2,5-trimethylhexane

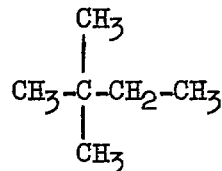


were recorded in an earlier report (ref. 1). This compound was investigated further because of its similarity to isooctane; it differs only in having an additional methylene group. The reactions of this compound, as well as of the other hydrocarbons discussed in this report, were conducted in a 1/16-inch-inside-diameter glass reactor tube. As shown in table I, in the initial stages of the oxidation of 2,2,5-trimethylhexane at 450° C and at short contact times a high ratio of organic peroxides to hydrogen peroxide is obtained, and in this respect the oxidation

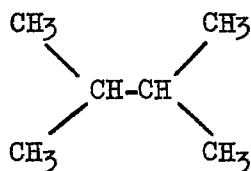
resembles that of n-heptane. Similarity to isooctane is also noted in the early stages; the yield of olefins exceeds the yield of carbonyl compounds (see reaction 1, table I). At higher temperatures and longer contact times the yield of hydrogen peroxide increases and is greater than that of organic peroxides, while the carbonyl formation increases rapidly. These later stages are characteristic of the oxidation path of isooctane. This is to be expected because of the similarity in chemical structure of the two hydrocarbons and because of the lessening of the selective action of the primary, secondary, and tertiary C-H bonds at the higher temperatures.

A comparison of the effect of contact time on the product distribution from the oxidation of 2,2,5-trimethylhexane and isooctane at 550° C is shown in figure 2. The rate of olefin and hydrogen-peroxide production is about the same for both compounds although the absolute quantities are larger for the nonane. The most striking difference in behavior of the two compounds is the large amount of carbonyl formation from 2,2,5-trimethylhexane, a phenomenon characteristic of the oxidation of straight chain hydrocarbons. These data afford additional evidence that the relative resistance to oxidative attack for these three hydrocarbons is isooctane > 2,2,5-trimethylhexane > n-heptane.

2,2-Dimethylbutane.- Data pertaining to the vapor-phase oxidation of 2,2-dimethylbutane

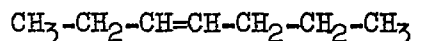


are shown in table II. Like isooctane and isobutane, this hydrocarbon requires high temperatures for appreciable oxidative attack; this is to be expected in accordance with the structural similarities of the three hydrocarbons. One also would predict from the relative number of primary C-H bonds in 2,2-dimethylbutane that its resistance to oxidation should lie between isobutane and isooctane; this was found to be the case. 2,2-Dimethylbutane is less resistant to attack than isobutane (cf. table II with table III) and is slightly more resistant than isooctane. However, this latter difference is difficult to evaluate since the data for 2,2-dimethylbutane are at 500° C and those for comparable contact times with isooctane are at 550° C (ref. 1). The ratio of hydrogen peroxide to organic peroxide is low (approximately 0.5 and 1.5 from reactions 1 and 2, respectively, in table II), in the initial stages of oxidation, in contrast with that for isooctane and isobutane. The higher ratio is reached only at longer contact times (reaction 3, table II). At shorter contact times (reactions 1 and 2), the olefin yield is high and the carbonyl yield is low; both results are similar to those obtained with isobutane.

2,3-Dimethylbutane. - The 2,3-dimethylbutane

shows oxidation characteristics similar to 2,2-dimethylbutane. Table IV summarizes preliminary data recorded for this compound. As with other compounds that are attacked appreciably only at high temperatures, 2,3-dimethylbutane yields mainly hydrogen peroxide and olefins in the initial oxidation processes. The ratio of hydrogen peroxide to organic peroxide is about equal to or greater than 1, being of the same order of magnitude as the 2,2 isomer. As expected from the highly branched nature of the hydrocarbons, the carbonyl compounds found with both the 2,3- and the 2,2-dimethylbutane are mainly ketones.

Comparison of 2,2-dimethylbutane and 2,3-dimethylbutane. - Since 2,2-dimethylbutane and 2,3-dimethylbutane are isomeric and differ only in the number of secondary and tertiary C-H bonds, a comparison of their behavior was of interest. 2,2-Dimethylbutane has two secondary and no tertiary C-H bonds, and 2,3-dimethylbutane has two tertiary and no secondary C-H bonds, while both have the same number of methyl groups. The initial experiments with these two compounds at 500° C and 0.08-second contact time (reaction 2, table II, and reaction 1, table IV) show that the extent of oxidative attack and the nature of the products formed are similar. However, 2,3-dimethylbutane is slightly more resistant to oxidation, as evidenced by the lower yield of products. This is in contrast with predictions based on the relative reactivities of secondary and tertiary C-H bonds in the combustion of paraffins as outlined in reference 6. The reason for this anomaly probably lies in the steric arrangement of the methyl groups in the two structures. The secondary hydrogen atoms in the 2,2-isomer are exposed while the tertiary hydrogen atoms must be in a trans configuration for maximum freedom from overcrowding. In this configuration the shielding effect of the methyl groups is the greatest. The qualitative results herein reported agree with the work of Cullis and Hinshelwood (ref. 7) who have shown the relative rates of oxidation of the 2,2- and 2,3-isomers to be 12 and 1, respectively.

3-Heptene. - Results obtained from the oxidation of 3-heptene

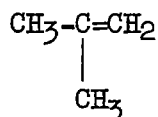
are summarized in table V. The contact time was held constant at 0.04 second and the temperature was varied. The molar ratio of oxygen

to hydrocarbon was 10:1. The greater resistance of 3-heptene to oxidative attack as compared with n-heptane is evident from a study of table V and is shown in figure 3. The data for n-heptane were taken from those reported in previous work on the program (ref. 1). In each reaction mixture, under the same conditions of temperature and contact time, the yield of oxidation products is less with the olefin. A striking feature of n-heptane reaction is the more than a hundredfold increase in extent of reaction exhibited on raising the temperature from 350° to 400° C. This phenomenon also occurs with 3-heptene, but to a lesser degree and through a range 50° C higher, 400° to 450° C. Beatty and Edgar (ref. 8) report that the initial oxidation of 3-heptene begins 56° C higher than that of n-heptane, when a reaction tube with 1-inch inside diameter is used. The smaller surface-to-volume ratio of their tube provides a less sensitive control of reaction than the use of a 1/16-inch-inside-diameter tube, and undoubtedly their observed "initial oxidation" corresponds to the sharp rise in product yield reported here.

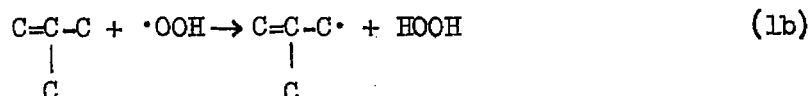
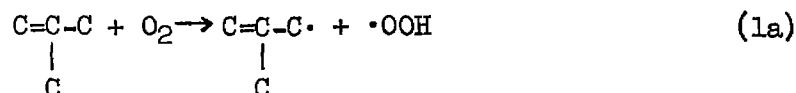
At 350° C n-heptane and 3-heptene both give greater yields of organic peroxides than of hydrogen peroxide, but the ratio is much greater with the paraffin. At higher temperatures where the reactivity of the oxygen has increased appreciably, the initiation reaction is more extensive and hydrogen peroxide is formed in larger quantities than the organic peroxides (see ref. 1, p. 13). As with the n-heptane, the formation of large amounts of carbonyl compounds from 3-heptene indicates less selectivity and a more general degradation than with the highly branched hydrocarbons. Olefin determinations with 3-heptene were not attempted.

The greater resistivity of 3-heptene than of n-heptane to vapor-phase oxidation is at variance with their relative ease of oxidation at room temperature. The latter results from the reactivity of the allylic C-H bonds of the olefin under conditions where the other secondary C-H bonds are substantially inert. However, it appears that at higher temperatures the reactivity of the C-H bonds all along the chain approaches that of the allylic C-H. There would then seem to be two major reasons for the greater reactivity of the paraffin at these higher temperatures: (1) The greater number of secondary hydrogen atoms, and therefore a statistically greater number of points vulnerable to attack, and (2) the resonance stabilization in radicals such as $R-\dot{C}H-CH=CH-R' \leftrightarrow R-CH=CH-\dot{C}H-R'$, and therefore their lower reactivity (ref. 9).

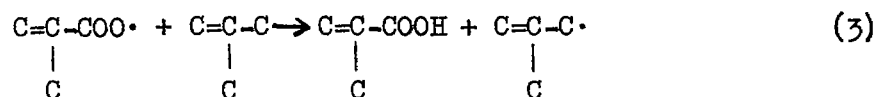
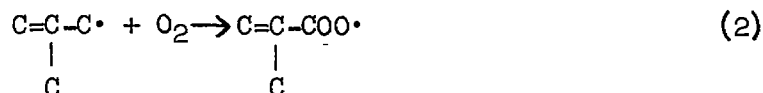
Isobutene.-- Some preliminary runs were made with isobutene



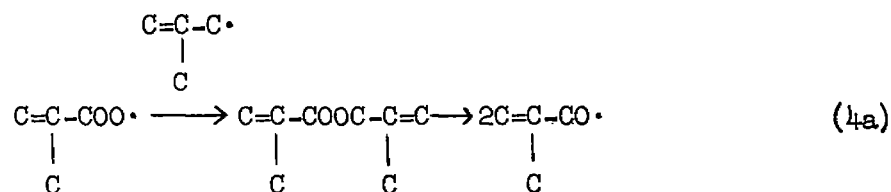
in order to compare the behavior of this olefin with that of the corresponding saturated hydrocarbon, isobutane. The results are reported in table III and in figure 4. Some of the data in table III were taken from previous work on this program (see ref. 1). A temperature of 550° C was necessary for any appreciable oxidation to occur at contact times of 0.08 and 0.16 second. The most noticeable difference between reaction of the two compounds is in the oxidation products. While isobutane yields both organic and hydrogen peroxides, only hydrogen peroxide is found with isobutene. Also, the only carbonyl compound formed in the partial oxidation of isobutene is formaldehyde, whereas only half of the quantity of carbonyl compounds from isobutane is formaldehyde; the other half is most probably acetone and isobutyraldehyde. A possible mechanism for the oxidation of isobutene consistent with these facts is as follows:

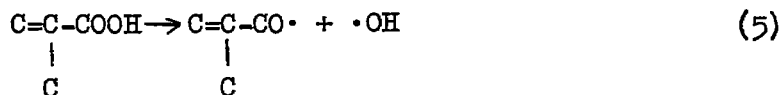
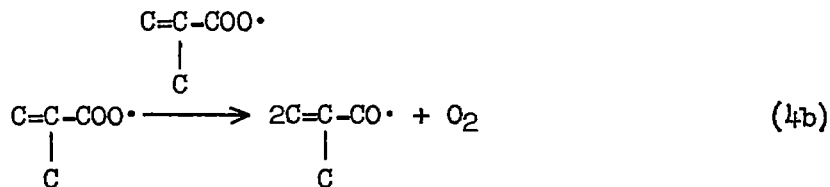


At 550° C the activity of the oxygen molecule is great and free radical initiations (1a) and (1b) account for the abundance of hydrogen peroxide. Further reaction with oxygen of the free radical formed could possibly involve chain propagation, as in equations (2) and (3):

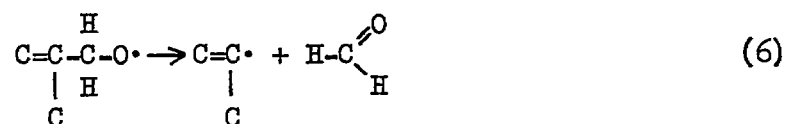


However, the hydroperoxide formed according to equation (3) would be very unstable (if formed at all) because of the high temperature, and indeed no alkyl hydroperoxide is found in the experimental studies. In accordance with the work of Rust, Vaughan, et al. (ref. 10), the alkylperoxy radical and any alkyl hydroperoxide no doubt would decompose to the alkoxy radical (eqs. (4a), (4b), and (5)):





Formaldehyde arises from the decomposition of this alkoxy radical as in equation (6):



The fate of the subsequent free radical from equation (6) is more doubtful. Bretton, Wan, and Dodge (ref. 11) indicate that the radical reacts with more oxygen and ultimately forms acetic acid and a second molecule of formaldehyde. These products correspond well with those detected in the present determinations.

The data shown in table III for isobutene are too limited to show any clear difference in the relative ease of oxidation of isobutene and isobutane. The results obtained, however, indicate a slightly greater resistance for isobutane. This would be consistent with the relative spontaneous ignition temperatures of polyisobutylenes and hydrogenated polyisobutylenes (ref. 12) and with the effect of unsaturation on the critical compression ratios of highly branched hydrocarbons (ref. 6).

Effect of Ratio of Surface to Volume

As pointed out earlier, the 1/16-inch-inside-diameter glass reactor tube has been employed in order to make use of the "wall effect" for quenching the reaction in its initial stages. While this procedure was quite successful, it was desirable to study the same oxidation in a larger reaction tube to obtain some quantitative measure of the effect of surface-to-volume ratio on the nature and extent of the reaction. Therefore an experiment on isooctane was conducted substituting a 1/4-inch-inside-diameter glass tube for the 1/16-inch-inside-diameter tube. Results obtained with the 1/4-inch tube are compared with those of the 1/16-inch tube in table VI, employing a stoichiometric oxygen-isooctane mixture at 450° C and 0.68-second contact time. It is evident from

these data that the initial reaction occurring in 1/16- and 1/4-inch reaction tubes is substantially the same. As expected, the extent of reaction increases with increasing tube size, that is, decreasing surface-to-volume ratio. In attempting a further comparison between these tubes, isooctane was oxidized at 550° C and 0.24-second contact time. Whereas the 1/16-inch glass tube enabled controlled reactions at this temperature, explosive reactions resulted with the 1/4-inch tube. In view of this, no attempts were made to employ the 1/4-inch tube with hydrocarbons which ignite in the low-temperature region, for example, n-heptane.

The suitability of the 1/4-inch reactor at 450° C and its unsuitability at 550° C also give additional significance to spontaneous-ignition-temperature measurements. Thus, while differences in the reaction chamber used for determining spontaneous ignition temperature and the present oxidation tube prevent any but qualitative comparison, it is noteworthy that isooctane undergoes spontaneous ignition at about 450° C in a 125-cubic-centimeter flask (ref. 13) but at about 500° C in a 43-cubic-centimeter ignition chamber (ref. 14). Extrapolation would suggest a spontaneous ignition temperature in small-diameter tubes in the 550° to 600° C range. Present results indicated that isooctane undergoes an almost instantaneous autoignition in a 1/4-inch tube at 550° C, while there is an appreciable induction period at 550° C in the 1/16-inch tube. At 450° C, the induction period in a 1/4-inch tube is sufficient to permit considerable reaction without explosion. These results serve to emphasize the importance of a high surface-to-volume ratio in obtaining controlled vapor-phase oxidation.

CONCLUSIONS

From the investigation of reaction processes leading to spontaneous ignition of hydrocarbons the following conclusions can be drawn:

1. The effect of adding a methylene group to a highly branched hydrocarbon is to reduce its resistance to oxidation; for a given set of reaction conditions, the relative amounts of organic peroxide and of carbonyl compounds increase, and the over-all yields of oxidation products are higher.
2. In the oxidation of isomeric branched hydrocarbons, the difference in resistance to oxidation is dependent upon the difference in structural configuration. While, in general, ease of oxidation of C-H bonds increases in the order primary < secondary < tertiary, steric effects may outweigh normal reactivity considerations.
3. n-Olefins are more resistant to vapor-phase oxidation than the corresponding paraffins. Highly branched olefins appear somewhat less

resistant to vapor-phase oxidation than the corresponding paraffins. However, insufficient data are available to permit any broad generalizations among these compounds.

4. The major products obtained in the oxidation of 3-heptene at lower temperatures (350° to 450° C) are similar to those obtained with n-heptane in the same temperature range but are produced in smaller amounts. Resonance stabilization in the radical and the fewer number of C-H bonds available for attack are suggested as reasons for the greater resistance of the n-olefins to oxidative attack.

5. Major products obtained during the initial stages of the oxidation of isobutene are hydrogen peroxide and formaldehyde.

6. The order of resistance to oxidation of the hydrocarbons for which comparable data are available is isobutane > isobutene > isooctane > 2,2,5-trimethylhexane > 3-heptene > n-heptane.

7. The extent of a vapor-phase oxidation increases with decreasing surface-to-volume ratio if other factors remain constant. The "wall effect" provided by a large surface-to-volume ratio is very helpful in maintaining reaction control in high-temperature vapor-phase oxidation.

University of Cincinnati,
Cincinnati, Ohio, December 2, 1953.

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TABLE I.- OXIDATION OF 2,2,5-TRIMETHYLHEXANE

Reaction mixture number	1	2	3	4	5	6	7
Conditions:							
Composition, mole hydrocarbon/moles							
oxygen	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Temperature, °C	450	450	450	450	550	550	550
Contact time, sec	0.04	0.08	0.16	0.24	0.04	0.08	0.16
Product analysis:							
Hydrogen peroxide, millimoles/mole							
2,2,5-trimethylhexane charged	0.03	0.6	17	39	4.7	7.5	11
Organic peroxides, millimoles/mole							
2,2,5-trimethylhexane charged	2.0	1.2	----	3.7	1.8	4.3	6.4
Olefin, millimoles/mole							
2,2,5-trimethylhexane charged	0.40	5.3	13	7.8	4.4	6.1	28
Total carbonyl, millimoles/mole							
2,2,5-trimethylhexane charged	Trace	24	51	180	22	70	----
Formaldehyde, millimoles/mole							
2,2,5-trimethylhexane charged	None	1.5	15	33	0.9	6.8	12
Acid, millimoles/mole							
2,2,5-trimethylhexane charged	None	3.0	7.3	15	0.3	2.8	9.4

TABLE II.- OXIDATION OF 2,2-DIMETHYLBUTANE

Reaction mixture number	1	2	3
Conditions:			
Composition, mole hydrocarbon/moles			
oxygen	0.11	0.11	0.11
Temperature, °C	500	500	500
Contact time, sec	0.04	0.08	0.16
Product analysis:			
Hydrogen peroxide, millimoles/mole			
2,2-dimethylbutane charged	0.20	1.2	19
Organic peroxides, millimoles/mole			
2,2-dimethylbutane charged	0.37	0.8	0.25
Olefin, millimoles/mole			
2,2-dimethylbutane charged	1.5	3.6	12
Total carbonyl, millimoles/mole			
2,2-dimethylbutane charged	Trace	0.73	73
Formaldehyde, millimoles/mole			
2,2-dimethylbutane charged	Trace	0.23	33
Acid, millimoles/mole			
2,2-dimethylbutane charged	None	0.40	7.8

TABLE III.- OXIDATION OF ISOBUTENE AND ISOBUTANE

	Isobutene		Isobutane	
Reaction mixture number	1	2	1	2
Conditions:				
Composition, mole hydrocarbon/mole oxygen	0.17	0.17	0.15	0.15
Temperature, °C	550	550	550	550
Contact time, sec	0.08	0.16	0.08	0.16
Analysis:				
Hydrogen peroxide, millimoles/mole hydrocarbon charged	1.8	3.3	1.2	3.6
Organic peroxide, millimoles/mole hydrocarbon charged	None	None	0.6	0.8
Olefin, millimoles/mole hydrocarbon charged	(a)	(a)	^b 2.5	^b 5.6
Total carbonyl, millimoles/mole hydrocarbon charged	3.1	----	^b 0.2	^b 0.8
Formaldehyde, millimoles/mole hydrocarbon charged	3.1	5.9	^b 0.1	^b 0.4
Acid, millimoles/mole hydrocarbon charged	0.8	0.6	----	----

^aNot determined.^bApproximate value.

TABLE IV.- OXIDATION OF 2,3-DIMETHYLBUTANE

Reaction mixture number	1	2
Conditions:		
Composition, mole hydrocarbon/mole oxygen	0.11	0.11
Temperature, °C	500	500
Contact time, sec	0.08	0.16
Product analysis:		
Hydrogen peroxide, millimoles/mole		
2,3-dimethylbutane charged	0.57	2.0
Organic peroxides, millimoles/mole		
2,3-dimethylbutane charged	0.76	1.2
Olefin, millimoles/mole		
2,3-dimethylbutane charged	2.9	1.3
Total carbonyl, millimoles/mole		
2,3-dimethylbutane charged	Trace	5.0
Formaldehyde, millimoles/mole		
2,3-dimethylbutane charged	Trace	0.18
Acid, millimoles/mole		
2,3-dimethylbutane charged	None	None

TABLE V.- OXIDATION OF 3-HEPTENE AND n-HEPTANE

	3-heptene			n-heptane		
Reaction mixture number	1	2	3	1	2	3
Conditions:						
Composition, mole hydrocarbon/mole oxygen	0.10	0.10	0.10	0.09	0.09	0.09
Temperature, °C	350	400	450	350	400	450
Contact time, sec	0.04	0.04	0.04	0.04	0.04	0.04
Product analysis:						
Hydrogen peroxide, millimoles/mole hydrocarbon charged	0.56	3.3	27	0.3	63	79
Organic peroxides, millimoles/mole hydrocarbon charged	0.64	.21	4.5	9.1	11.3	2.1
Olefin, millimoles/mole hydrocarbon charged	(a)	(a)	(a)	2.9	58	78
Total carbonyl, millimoles/mole hydrocarbon charged	Trace	15	220	----	----	----
Aldehyde, millimoles/mole hydrocarbon charged	Trace	9.4	110	2.6	360	360
Acid, millimoles/mole hydrocarbon charged	None	1.7	28	4.0	57	60

^aNot determined.

TABLE VI.- COMPARISON OF RESULTS OF ISOOCTANE OXIDATION
IN REACTION TUBES OF DIFFERENT DIAMETERS

Reaction-tube diameter, in.	1/16	1/4
Conditions:		
Composition, mole hydrocarbon/mole oxygen	0.08	0.08
Temperature, °C	450	450
Contact time, sec	0.68	0.68
Analysis:		
Hydrogen peroxide, millimoles/mole hydrocarbon charged	14.7	47
Organic peroxides, millimoles/mole hydrocarbon charged	1.4	----
Olefin, millimoles/mole hydrocarbon charged	46	58
Total carbonyl, millimoles/mole hydrocarbon charged	35	74
Formaldehyde, millimoles/mole hydrocarbon charged	12	17
Acid, millimoles/mole hydrocarbon charged	6.5	12

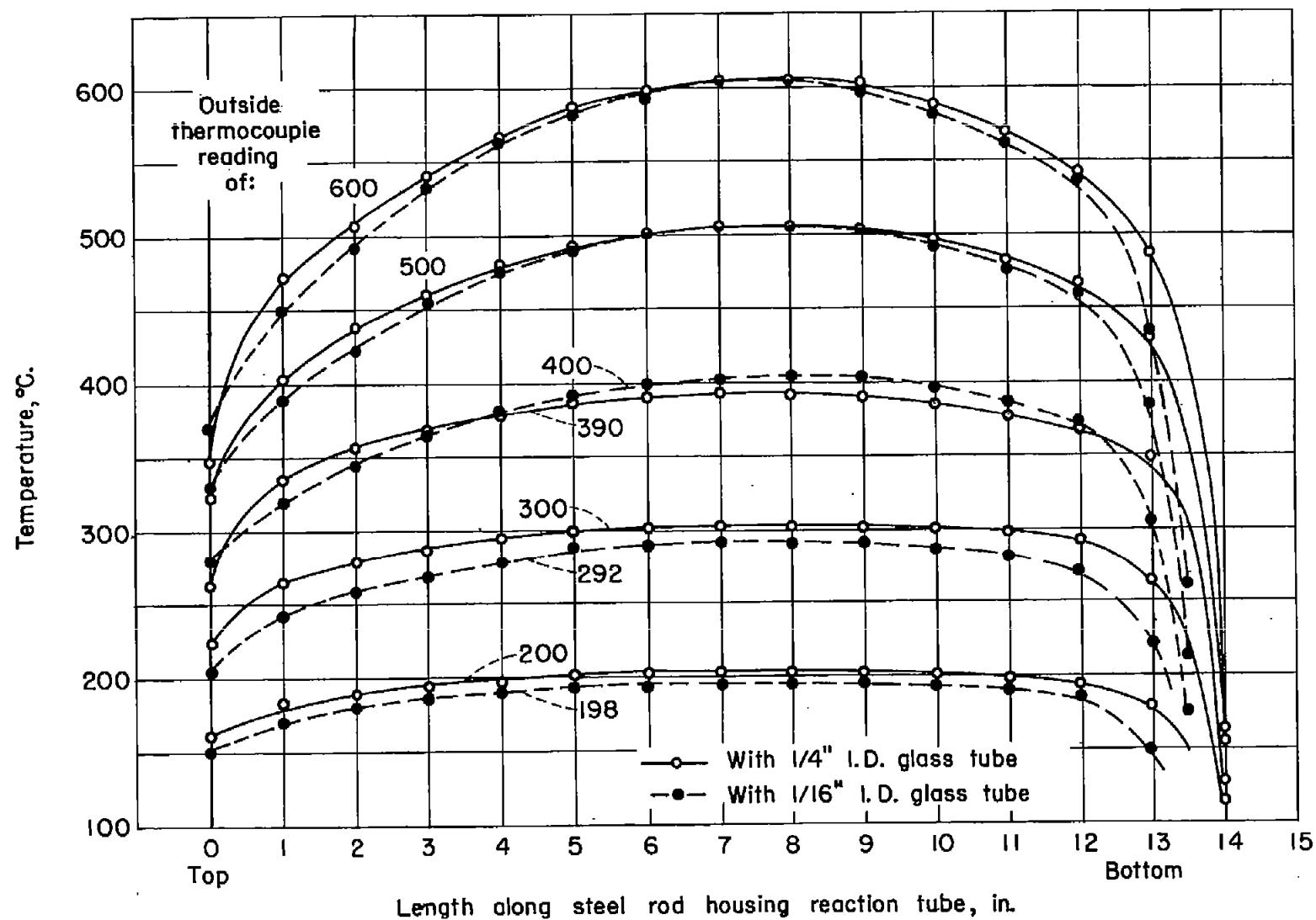


Figure 1.- Temperature distribution in 13-inch-long glass reactor tubes having 1/4- and 1/16-inch inside diameters. Zero airflow rate.

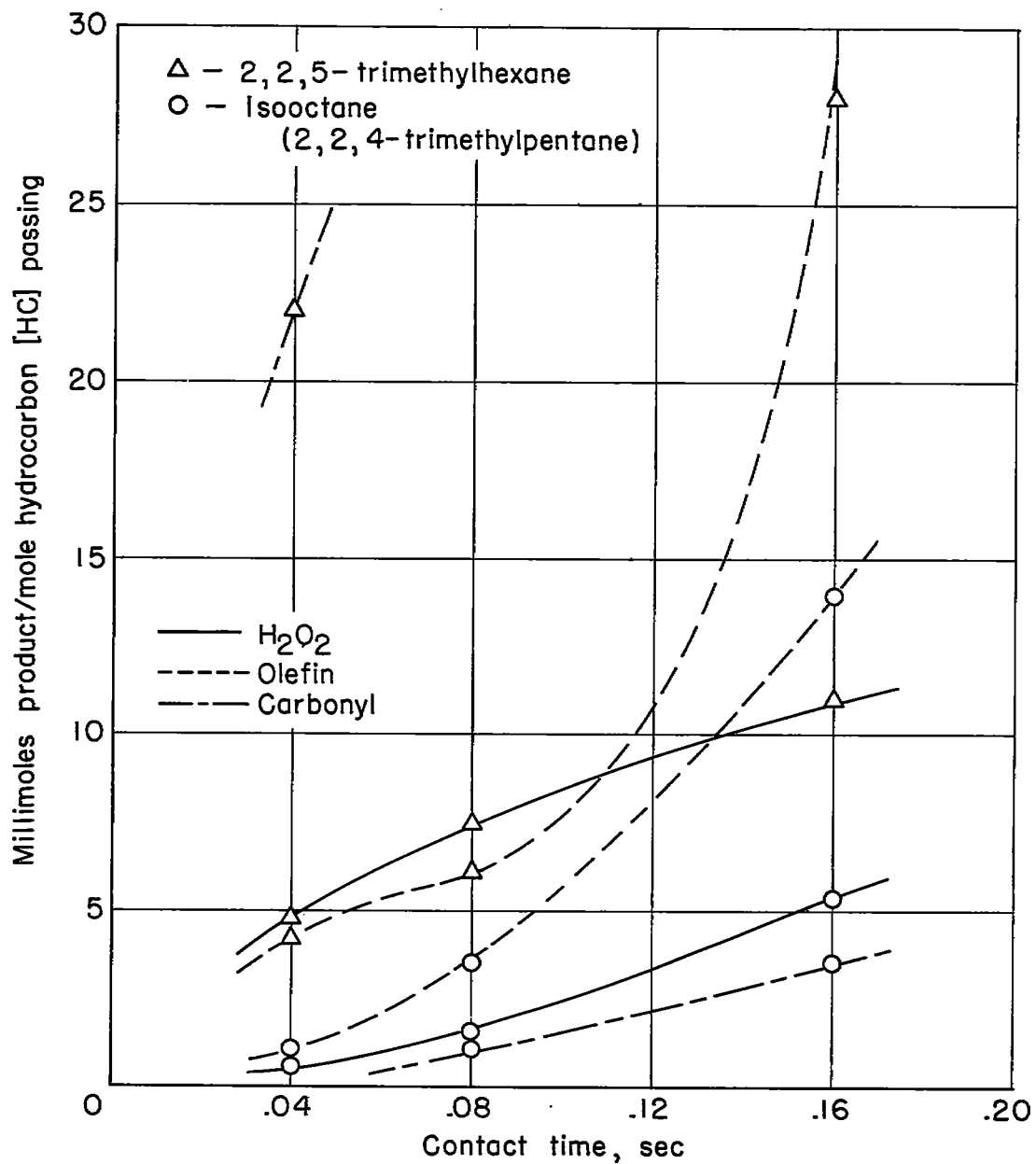


Figure 2.- Comparison of oxidation products of isooctane and 2,2,5-trimethylhexane at 550° C.

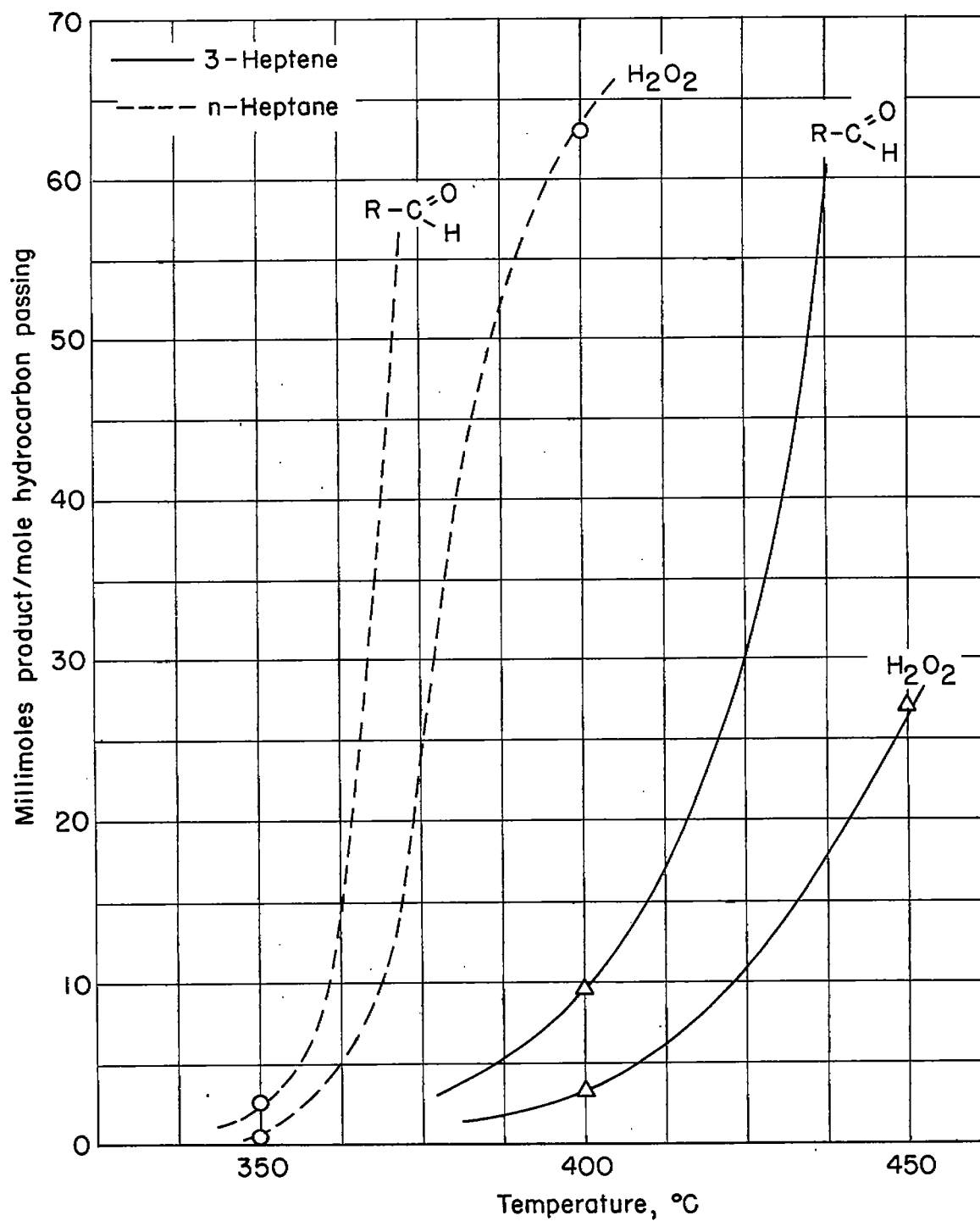


Figure 3.- Comparison of oxidation products of 3-heptene and n-heptane.

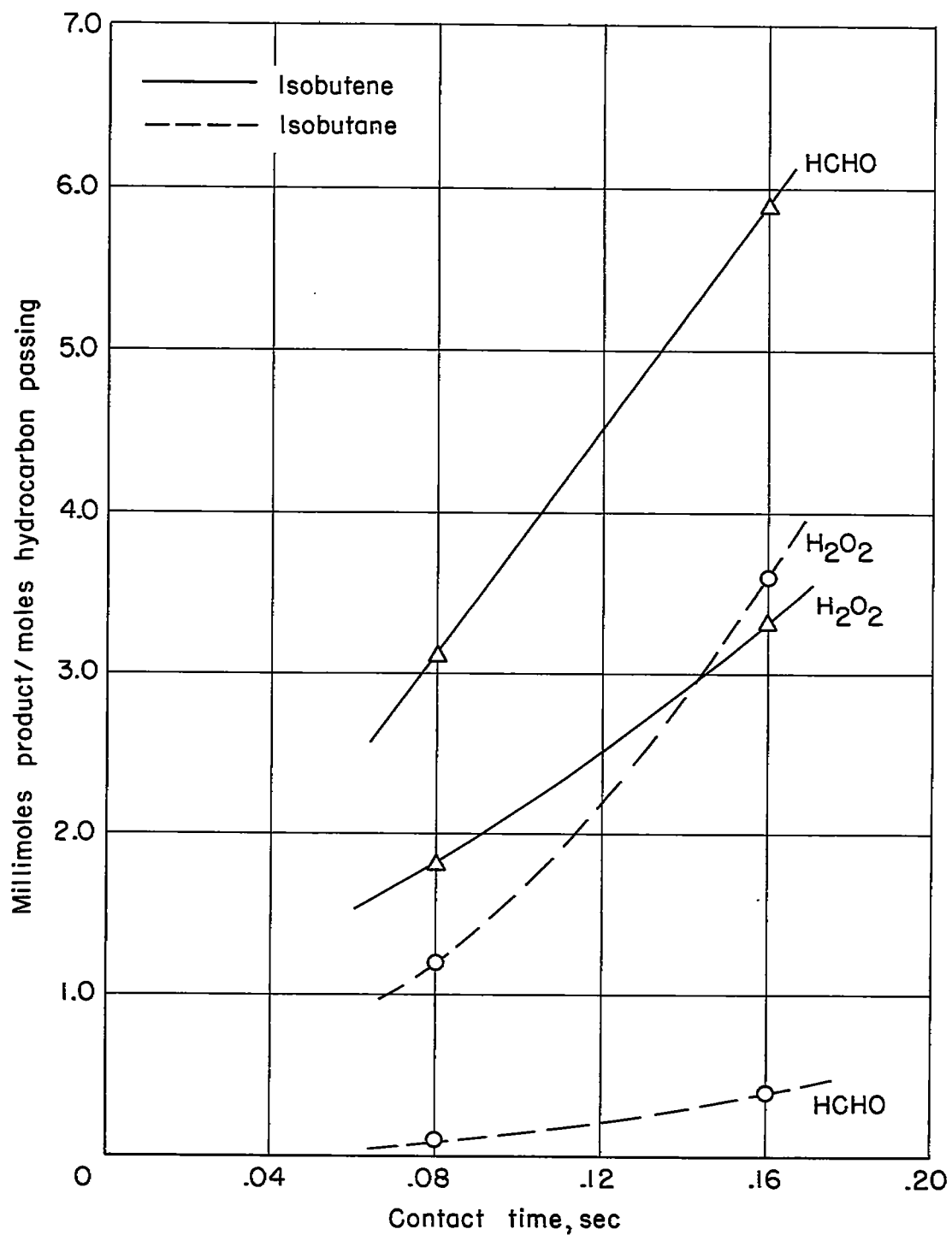


Figure 4.- Comparison of oxidation products of isobutene and isobutane at 550° C.